



THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: April 10, 2006

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

AFFIDAVIT OF DENNIS NEWNS

UNDER 37 C.F.R. 1.132

Sir:

I, Dennis Newns, declare that:

1. I received a B. A. degree in Chemistry form Oxford University United Kingdom in 1964 and a Ph.D. degree in Theoretical Physical Chemistry form the University of London in 1967.

2. I am a theoretical solid state scientist. My resume and curriculum vitae are attached.
3. The USPTO response dated October 20, 2005 at page 4 regarding the subject application cites Schuller et al "A Snapshot View of High Temperature Superconductivity 2002" (report from workshop on High Temperature Superconductivity held April 5-8, 2002 in San Diego) which the examiner states "discusses both the practical applications and theoretical mechanisms relating to superconductivity."
4. The Examiner at page 4 of the Office Action cites page 4 of Schuller et al which states:

"Basic research in high temperature superconductivity, because the complexity of the materials, brings together expertise from materials scientists, physicists and chemists, experimentalists and theorists... It is important to realize that this field is based on complex materials and because of this materials science issues are crucial. Microstructures, crystallinity, phase variations, nonequilibrium phases, and overall structural issues play a crucial role and can strongly affect the physical properties of the materials. Moreover, it seems that to date there are no clear-cut directions for searches for new superconducting phases, as shown by the serendipitous discovery of superconductivity in MgB_2 . Thus studies in which the nature of chemical bonding and how this arises in existing superconductors may prove to be fruitful. Of course, "enlightened" empirical searches either guided by chemical and

materials intuition or systematic searches using well-defined strategies may prove to be fruitful. It is interesting to note that while empirical searches in the oxides gave rise to many superconducting systems, similar (probable?) searches after the discovery of superconductivity in MgB_2 have not uncovered any new superconductors. "

5. The Examiner at pages 4 -5 of the Office Action cites pages 5- 6 of Schuller et al which state:

"The theory of high temperature superconductivity has proven to be elusive to date. This is probably as much caused by the fact that in these complex materials it is very hard to establish uniquely even the experimental phenomenology, as well as by the evolution of many competing models, which seem to address only particular aspects of the problem. The Indian story of the blind men trying to characterize the main properties of an elephant by touching various parts of its body seems to be particularly relevant. It is not even clear whether there is a single theory of superconductivity or whether various mechanisms are possible. Thus it is impossible to summarize, or even give a complete general overview of all theories of superconductivity and because of this, this report will be very limited in its theoretical scope."

6. The Examiner at page 5 of the Office Action cites page 7 of Schuller et al which states:

"Thus far, the existence of, a totally new superconductor has proven impossible to predict from first principles. Therefore their discovery has been based largely on empirical approaches, intuition, and, even serendipity. This unpredictability is at the root of the excitement that the condensed matter community displays at the discovery of a new material that is superconducting at high temperature."

7. I am submitting this declaration to clarify what is meant by predictability in theoretical solid state science. All solid state materials, even elemental solids, present theoretical problems. That difficulty begins with the basic mathematical formulation of quantum mechanics and how to take into account all interactions that are involved in atoms having more than one electron and where the interactions between the atoms may be covalent, ionic or Van der Waals interactions. A theory of a solid is based on approximate mathematical formalisms to represent these interactions. A theoretical solid state scientist makes an assessment using physical intuition, mathematical estimation and experimental results as a guide to focus on features of the complex set of interactions that this assessment suggests are dominate in their effect on the physical phenomena for which the theorist is attempting to develop a theory. This process results in what is often referred to as mathematical formalism. This formalism is then applied to specific examples to determine whether the formalism produces computed results that agree with measured experimental results. This process can be considered a "theoretical experiment." For example, applying the theoretical formalism to a particular crystal

structure comprised of a particular set of atoms to compute a value of a desired property is in this context a "theoretical experiment."

8. Even when a successful theoretical formalism is developed, that formalism does not produce a list of materials that have a particular property that is desired. Rather for each material of interest the same "theoretical experiment" must be conducted. Moreover, even if such a "theoretical experiment" indicates that the particular material investigated has the property, there is no assurance that it does without experimentally fabricating the material and experimentally testing whether it has that property.
9. For example, semiconductors have been studied both experimentally and theoretically for more than 50 years. The theory of semiconductors is well understood. A material is a semiconductor when there is a filled valence band that is separated from the next empty or almost empty valence band by an energy that is of the order of the thermal energy of an electron at ambient temperature. The electrical conductivity of the semiconductor is controlled by adding dopants to the semiconductor crystal that either add electrons to the empty valence band or remove electrons from the filled valence band. Notwithstanding this theoretical understanding of the physical phenomena of semiconductivity, that understanding does not permit either a theoretical or experimental solid state scientist to know *a priori* what materials will in fact be a semiconductor. Even with the well developed semiconductor theoretical formalisms, that theory cannot be asked the question "can you list for me all materials that will be a semiconductor?" Just as an experimentalist must do, the theoretical scientist must select a particular material for

examination. If the particular material already exists an experimentalist can test that material for the semiconducting property. If the particular material does not exist, the theoretical solid state scientist must first determine what the crystal structure will be of that material. This in of itself may be a formidable theoretical problem to determine accurately. Once a crystal structure is decided on, the theoretical formalism is applied in a "theoretical experiment" to determine if the material has the arraignment of a fully filled valence and an empty valence band with the correct energy spacing. Such a theoretical experiment generally requires the use of a computer to compute the energy band structure to determine if for the selected composition the correct band configuration is present for the material to be a semiconductor. This must be verified by experiment. Even with the extensive knowledge of semiconducting properties such computations are not 100% accurate and thus theory cannot predict with 100% accuracy what material will be a semiconductor. Experimental confirmation is needed. Moreover, that a theoretical computation is a "theoretical experiment" in the conceptual sense not different than a physical experiment. The theorist starting out on a computation, just as an experimentalist staring out on an experiment, has an intuitive feeling that, but does not know whether, the material studied will in fact be a semiconductor. As stated above solid state scientists, both theoretical and experimental, are initially guided by physical intuition based on prior experimental and theoretical work. Experiment and theory complement each other, at times one is ahead of the other in an understanding of a problem, but which one is ahead changes over time as an understanding of the physical phenomena develops.

10. This description of the semiconductor situation is for illustration of the capability of theory in solid state science where there is a long history of both experimental and theoretical developments.
11. Superconductivity was first discovered by H. Kammerlingh Onnes in 1911 and the basic theory of superconductivity has been known many years before Applicants' discovery. For example, see the book "Theory of Superconductivity", M. von Laue, Academic Press, Inc., 1952 (See Attachment AD of the Third Supplementary Amendment dated March 1, 2005). Prior to applicants' discovery superconductors were grouped into two types: Type I and Type II.
12. The properties of Type I superconductors were modeled successfully by the efforts of John Bardeen, Leon Cooper, and Robert Schrieffer in what is commonly called the BCS theory. A key conceptual element in this theory is the pairing of electrons close to the Fermi level into Cooper pairs through interaction with the crystal lattice. This pairing results from a slight attraction between the electrons related to lattice vibrations; the coupling to the lattice is called a phonon interaction. Pairs of electrons can behave very differently from single electrons which are fermions and must obey the Pauli exclusion principle. The pairs of electrons act more like bosons which can condense into the same energy level. The electron pairs have a slightly lower energy and leave an energy gap above them on the order of .001 eV which inhibits the kind of collision interactions which lead to ordinary resistivity. For temperatures such that the thermal energy is less than the band gap, the material exhibits zero resistivity.

13. There are about thirty pure metals which exhibit zero resistivity at low temperatures and have the property of excluding magnetic fields from the interior of the superconductor (Meissner effect). They are called Type I superconductors. The superconductivity exists only below their critical temperatures and below a critical magnetic field strength. Type I and Type II superconductors (defined below) are well described by the BCS theory.
14. Starting in 1930 with lead-bismuth alloys, a number of alloys were found which exhibited superconductivity; they are called Type II superconductors. They were found to have much higher critical fields and therefore could carry much higher current densities while remaining in the superconducting state.
15. Ceramic materials are expected to be insulators -- certainly not superconductors, but that is just what Georg Bednorz and Alex Muller, the inventors of the patent application under examination, found when they studied the conductivity of a lanthanum-barium-copper oxide ceramic in 1986. Its critical temperature of 30 K was the highest which had been measured to date, but their discovery started a surge of activity which discovered materials exhibiting superconducting behavior in excess of 125 K. The variations on the ceramic materials first reported by Bednorz and Muller which have achieved the superconducting state at much higher temperatures are often just referred to as high temperature superconductors and form a class of their own.
16. It is generally believed by theorists that Cooper pairs result in High T_c superconductivity. What is not understood is why the Cooper pairs remain together at the higher temperatures. A phonon is a vibration of the atoms about their

equilibrium positions in a crystal. As temperature increases these vibrations are more complex and the amplitude of these vibrations is larger. How the Cooper pairs interact with the phonons at the lower temperature, when these oscillations are less complex and of lower amplitude, is understood, this is the BCS theory. Present theory is not able to take into account the more complex and larger amplitude vibrations that occur at the higher temperatures.

17. The article of Schuller referred to by the Examiner in paragraphs 4, 5 and 6 present essentially the same picture.
18. In paragraph 4 above Schuller states "Of course, 'enlightened' empirical searches either guided by chemical and materials intuition or systematic searches using well-defined strategies may prove to be fruitful. It is interesting to note that while empirical searches in the oxides gave rise to many superconducting systems, similar (probable?) searches after the discovery of superconductivity in MgB_2 have not uncovered any new superconductors." Schuller is acknowledging that experimental researchers using intuition and systematic searches found the other known high T_c superconductors. Systematic searching is applying what is known to the experimental solid state scientist, that is, knowledge of how to fabricate compounds of the same class as the compounds in which Bednorz and Muller first discovered High T_c superconductivity. That a similar use of intuition and systematic searching "after the discovery of superconductivity in MgB_2 have not uncovered any new superconductors" is similar to a "theoretical experiment" that after the computation is done does not show that the material studied has the property being investigated, such as semiconductivity. The Schuller article was published in April 2002

approximately one year after the experimental discovery of superconductivity in MgB_2 was reported on in March 2001 (Reference 8 of the Schuller article. See paragraph 19 of this affidavit.) This limited time of only one year is not sufficient to conclude that systematic searching "after the discovery of superconductivity in MgB_2 " cannot uncover any new superconductors. Experimental investigations of this type are not more unpredictable than theoretical investigations since the experimental investigation has a known blue print or course of actions, just as does a "theoretical experiment." Just as an physical experimental investigation may lead to a null result a "theoretical experiment" may lead to a null result. In the field of High T_c superconductivity physical experiment is as predictable as a well developed theory since the experimental procedures are well known even though very complex. Experimental complexity does not mean the field of High T_c superconductivity is unpredictable since the methods of making these material are so well known.

19. In paragraph 4 above Schuler refers the discovery of MgB_2 citing the paper of Nagamatsu et al. Nature Vol. 410, March 2001 in which the MgB_2 is reported to have a T_c of 39 K, a layered graphite crystal structure and made from powders using know ceramic processing methods. MgB_2 has a substantially simpler structure than the first samples reported on my Bednorz and Muller and therefore can be more readily investigated theoretically. There have been recent reports by Warren Pickett of the University of California at Davis and by Marvin L. Cohen and Steven Louie at the University of California at Berkeley describing progress in a theoretical understanding of the T_c of MgB_2 . It is not surprising that progress in the theory of

superconductivity at 39 K has been made based on this relatively simple material.

In fact a few months after the Schuller article was published in April 2002 Marvin .L. Cohen and Steven Louie were authors on an article Choi, HJ; Roundy, D; Sun, H; Cohen, ML; Louie, SG "First-principles calculation of the superconducting transition in MgB_2 within the anisotropic Eliashberg formalism " PHYSICAL REVIEW B; JUL 1, 2002; Vol. 66; p 20513. The following is from the Abstract of this article:

" We present a study of the superconducting transition in MgB_2 using the ab initio pseudopotential density-functional method, a fully anisotropic Eliashberg equation, and a conventional estimate for μ^* . Our study shows that the anisotropic Eliashberg equation, constructed with ab initio calculated momentum-dependent electron-phonon interaction and anharmonic phonon frequencies, yields an average electron-phonon coupling constant $\lambda=0.61$, a transition temperature $T_c=39$ K, and a boron isotope-effect exponent $\alpha(B)=0.32$. The calculated values for T_c , λ , and $\alpha(B)$ are in excellent agreement with transport, specific-heat, and isotope-effect measurements, respectively. The individual values of the electron-phonon coupling $\lambda(k,k')$ on the various pieces of the Fermi surface, however, vary from 0.1 to 2.5. The observed T_c is a result of both the raising effect of anisotropy in the electron-phonon couplings and the lowering effect of anharmonicity in the relevant phonon modes." (Emphasis added)

Thus the statement of the Schuller article in paragraph 5 above "The theory of high temperature superconductivity has proven to be elusive to date" is not totally accurate since shortly after the publication of the Schuller article a theory of the T_c of MgB_2 was published by Marvin .L. Cohen and Steven Louie.

A month later they expanded on this in the article Choi, HJ; Roundy, D; Sun, H; Cohen, ML; Louie, SG "The origin of the anomalous superconducting properties of MgB_2 " NATURE, AUG 15, 2002; Vol 418; pp 758-760. The following is from the Abstract of this article:

" Magnesium diboride ... differs from ordinary metallic superconductors in several important ways, including the failure of conventional models ... to predict accurately its unusually high transition temperature, the effects of isotope substitution on the critical transition temperature, and its

anomalous specific heat A detailed examination of the energy associated with the formation of charge-carrying pairs, referred to as the 'superconducting energy gap', should clarify why MgB_2 is different. Some early experimental studies have indicated that MgB_2 has multiple gaps.... Here we report an ab initio calculation of the superconducting gaps in MgB_2 and their effects on measurable quantities. An important feature is that the electronic states dominated by orbitals in the boron plane couple strongly to specific phonon modes, making pair formation favourable. This explains the high transition temperature, the anomalous structure in the specific heat, and the existence of multiple gaps in this material. Our analysis suggests comparable or higher transition temperatures may result in layered materials based on B, C and N with partially filled planar orbitals. (Emphasis added)

Thus the statement in the Schuller article in paragraph 5 above "Thus far, the existence of, a totally new superconductor has proven impossible to predict from first principles" was shown by the work of Marvin L. Cohen and Steven Louie published shortly after the article of Schuller also to be not totally accurate.

20. In paragraph 5 above Schuller states "The theory of high temperature superconductivity has proven to be elusive to date." As stated above although solid state theorist believe that Cooper Pairs are the mechanism of the High T_c superconductors, we do not as of yet completely understand how to create a mathematical formalism that takes into account the atomic vibrations at these higher temperatures to theoretically permit that electrons to remain paired.

21. In paragraph 5 above Schuller further states "This is probably as much caused by the fact that in these complex materials it is very hard to establish uniquely even the experimental phenomenology." Even though these materials are complex that complexity does not have to be understood to make these material since experimental solid state scientists well understand the method of making these materials. The book "Copper Oxide Superconductors" by Charles P. Poole, Jr.,

Timir Datta and Horacio A. Farach, John Wiley & Sons (1998), [(See Attachment 23 of The Fifth Supplemental Amendment dated March 1, 2004)] referred to herein as Poole 1988 states in Chapter 5 entitled "Preparation and Characterization of Samples" states at page 59:

"Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials".

Poole et al. further states at page 61:

"In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor."

22. It is thus clear that experimentalists knew, at the time of Benor and Muller's discovery, how to make the High T_c class of material and that to do so it was not necessary to precisely understand the experimental phenomenology.
23. Charles Poole et al. published another book in 1995 entitled "Superconductivity" Academic Press which has a Chapter 7 on "Perovskite and Cuprate Crystallographic Structures". (See Attachment Z of the First Supplementary Amendment dated

March 1, 2005). This book will be referred to as Poole 1995. At page 179 of Poole 1995 states:

"V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics."

24. Thus Poole 1988 states that the high T_c superconducting materials "are not difficult to synthesize" and Poole 1995 states that "the new superconductors do indeed possess [the] characteristics" that Applicants' specification (the patent application currently under examination) describes these new superconductors to have.

25. In paragraph 5 above Schuller states:

"The theory of high temperature superconductivity has proven to be elusive to date. This iscaused by the fact ... the evolution of many competing models, which seem to address only particular aspects of the problem. The Indian story of the blind men trying to characterize the main properties of an elephant by touching various parts of its body seems to be particularly relevant. It is not even clear whether there is a single theory of superconductivity or whether various mechanisms are possible. Thus it is impossible to summarize, or even give a complete general overview of all theories of superconductivity and because of this, this report will be very limited in its theoretical scope."

The initial development of a theory always considers the problem from many different aspects until the best and most fruitful approach is realized. That at this time "It is not even clear whether there is a single theory of superconductivity or whether various mechanisms are possible" does not mean that experimental solid state scientists do not know how to make this class of High T_c materials. As stated by Poole 1988 and Poole 1995 the experimental solid state scientist does know how to make this class of High T_c materials.

26. The Examiner at page 5 of the Office Action cites page 7 of Schuller et al which states:

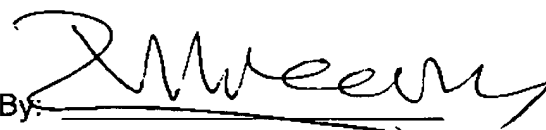
"Thus far, the existence of, a totally new superconductor has proven impossible to predict from first principles. Therefore their discovery has been based largely on empirical approaches, intuition, and, even serendipity. This unpredictability is at the root of the excitement that the condensed matter community displays at the discovery of a new material that is superconducting at high temperature."

A first principles theory that accurately predicts all physical properties of a material does not exist for as simple a material as water in its solid form as ice which may very well be the most extensively studied solid material. Most theories of solid state materials have phenomenological components that are approximations based on empirical evidence. As stated above solid state theoretical scientists have not as of yet formulated a theoretical formalism that accounts for electrons remaining paired as Cooper pairs at higher temperatures. But this does not prevent experimental scientists from fabricating materials that have structurally similar properties to the

materials first discovered by Bednorz and Muller. This is particularly true since the basic theory of superconductivity were also well known at the time of their discovery and the methods of making these materials was well known at the time of their discovery. It was not necessary at the time of their discovery to have the specific theoretical mechanism worked out in detail in order to make samples to test for High Tc superconductivity. Even Schuller acknowledges "empirical searches in the oxides gave rise to many superconducting systems."

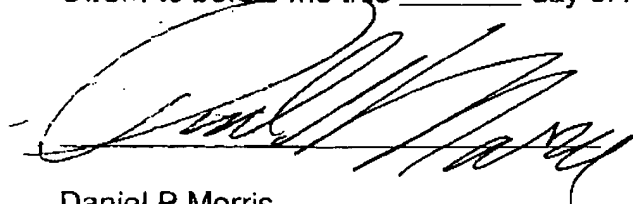
27. I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: 04/11/06

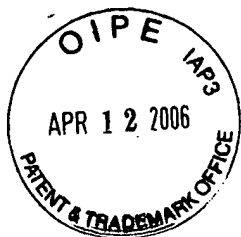
By: 

Dennis News

Sworn to before me this 11th day of April , 2006.


Daniel P Morris

DANIEL P. MORRIS
NOTARY PUBLIC, State of New York
No. 4888676
Qualified in Westchester County
Commission Expires March 16, ~~19~~ 2007



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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF GEORG BEDNORZ
UNDER 37 C.F.R. 1.132

Sir:

I, J.Georg Bednorz , declare that:

1. I am a coinventor of the referenced application.
2. I received a M. S. Degree in Minerology/Crystallography (1976) from the University of Muenster in Germany and a Ph.D. degree in Natural Science (1982) from the Swiss Federal Institute of Technology (ETH) in Zuerich - Switzerland.

3. The USPTO response dated October 20, 2005 at page 7 cites the following web page <http://www.nobelchannel.com/learningstudio/introduction.sps?id=295&eid=0>

Which states

It is worth noting that there is no accepted theory to explain the high-temperature behavior of this type of compound. The BCS theory, which has proven to be a useful tool in understanding lower-temperature materials, does not adequately explain how the Cooper pairs in the new compounds hold together at such high temperatures. When Bednorz was asked how high-temperature superconductivity works, he replied, "If I could tell you, many of the theorists working on the problem would be very surprised."

4. This declaration is to explain the meaning of the statement attributed to me "If I could tell you, many of the theorists working on the problem would be very surprised" in response to a question from the interviewer about the mechanism of High Tc superconductivity.

5. Following the discovery of the High Tc superconductivity in oxides by my coinventor Alex Mueller and me, the enormous research effort conducted by experimentalist specialized in different disciplines of solid state science created a very complex scenario. After our discovery new layered perovskite-like CuO-compounds with comparable and higher Tc were discovered of the type that are reported on in our original publication and that are described in our patent application. These new materials were made according to known principles of ceramic science that we described in our patent application. The rapid experimental developments were guided by previous work on materials having related the composition and structure. This enormous amount of new information collected over a short period of time made it hard to get a clear picture at that time of the experimental situation for both experimental specialists and theorists. In addition to showing superconductivity at temperatures higher than previously observed, this new information included novel and unusual properties, so far unexplained in the superconducting and normal state. I am an experimental scientist and in the field of solid state science, because of the complexities of theory and experiment, workers in the field are either experimentalist or theorist and typically not both. In this field, including the field of high Tc superconductivity, theory utilizes complex mathematical procedures about which theorists are experts. Thus theorists working in the field would have been surprised if, I, as an experimentalist, had been the sole person in the field to gain a sufficient overview and experimental and theoretical insight, to propose a final theory of high temperature superconductivity at this early stage of research.

6. I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date:

Feb. 24 / 2006

By:

J. Georg Bednorz
J. Georg Bednorz